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# Measurements of atmospheric hydroperoxides over a rural site in central Japan during summers using a helicopter

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## HIGHLIGHTS

- Concentrations of hydroperoxides as well as the concentrations of $O_3$, $SO_2$ and $NO_X$* in the high-altitude atmosphere were measured using a helicopter.
- Hydroperoxides in the high-altitude atmosphere were measured using an HPLC system in a laboratory within 5–10 min after sampling.
- The concentrations of hydroperoxides were highest in the atmosphere at altitudes of 6,000 to 8,000 ft.
- The potential capacity of $SO_2$ oxidation in the aqueous phase is large during summers over central Japan.

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## ABSTRACT

The concentrations of hydroperoxides ($H_2O_2$ and MHP), $O_3$, $SO_2$ and $NO_X$* over Imizu City, Toyama Prefecture, Japan were measured during summers using a helicopter. The concentrations of hydroperoxides were analyzed by an HPLC system within 5–10 min after the sampling. The $H_2O_2$ concentration was lowest at the surface, and the highest concentration was detected at altitudes of 6000 and 8000 ft. The MHP was also higher in the high-altitude atmosphere. Significantly high concentrations of hydroperoxides were observed when air pollutants were transported from China. The concentration of $H_2O_2$ was higher than that of $SO_2$ above 4000 ft where the potential capacity of $SO_2$ oxidation in the aqueous phase is large. A helicopter is useful for measuring of hydroperoxides in the high-altitude atmosphere using an HPLC system in a laboratory.



## 1. Introduction

Hydroperoxides (hydrogen peroxide and organic hydroperoxides) play an important role in radical chemistry in the gas-phase and aqueous-phase chemistry of acidic precipitation. Hydroperoxides such as hydrogen peroxide ($H_2O_2$) and methyl hydroperoxide ($CH_3OOH$, MHP) are produced through the self-reaction of peroxy radicals that are intimately linked to ozone ($O_3$) chemistry (e.g. Jackson and Hewitt, 1999; Lee et al., 2000; Vione et al., 2003). Hydroperoxides also play significant roles in atmospheric processes, such as $SO_2$ oxidation in liquid water and the formation of secondary organic aerosol (SOA); they also damage vegetation (e.g. Möller, 1989, 2009; Watanabe et al., 1999; Kume et al., 2001; Hua et al., 2008; Chen et al., 2010; Herckes et al., 2013).

Recently, the $O_3$ concentration in the background troposphere has significantly changed over East Asian countries (Akimoto et al., 1994; Tanimoto, 2009). According to Tanimoto (2009), an increase of approximately 1 ppb per year in the average concentration of $O_3$ was observed from 1998 to 2006 over Japan, especially in the spring when the background $O_3$ shows maximum concentrations in the middle to high latitudes (Watanabe et al., 2005). The change in the $O_3$ concentration may significantly affect the formation of hydroperoxides. Measuring hydroperoxides in the atmosphere at high elevations is important for evaluating the oxidative capacity of $SO_2$ in cloud water and effects harmful to the ecosystem at mountainous sites. However, there has been a shortage of gaseous hydroperoxide data in the high-altitude atmosphere over East Asian countries including Japan (Watanabe et al., 1995; Ren et al., 2009). In particular, vertical profiles of hydroperoxides have hardly been measured over Japan.

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Hydroperoxides in the high-altitude atmosphere have been measured many times over the United States and Europe (e.g., Kleinman and Daum, 1991; O'Sullivan et al., 2004; Snow et al., 2007; Klippel et al., 2011). Airborne measurements have usually been made using a fixed-wing aircraft, such as a Cessna plane (e.g., Kleinman and Daum, 1991; Hatakeyama et al., 2001; Watanabe et al., 2001a; Matsuki et al., 2003; Klippel et al., 2011; Nair et al., 2012; Maki et al., 2013; Srivastava et al., 2013). Many hydroperoxide measurements, especially airborne measurements, have been made mainly by a wet chemical system based on the technique described by Lazrus et al. (1986), using identical chemistry (peroxidase-catalyzed dimerization of *p*-hydroxyphenylacetic acid with fluorometric detection). The instrument is equipped with two channels. One channel delivers total hydroperoxides ($H_2O_2$ + organic hydroperoxides) while, in the other channel, $H_2O_2$ is selectively decomposed by catalase (organic hydroperoxides are delivered). The $H_2O_2$ mixing ratio is estimated based on the difference between total hydroperoxides and organic hydroperoxides. It is important to check the catalase efficiency (Lazrus et al., 1985, 1986; Ayers et al., 1996; Lee et al., 2000; Klippel et al., 2011).

To measure $H_2O_2$ exactly, it is best to analyze hydroperoxides in sampling solution immediately after collection using a high-performance liquid chromatography (HPLC) system to separate the $H_2O_2$ and organic hydroperoxides such as MHP from the total hydroperoxides (Hatakeyama et al., 1993; Kok et al., 1995; Morgan and Jackson, 2002; Takami et al., 2003). Usually, it is difficult to load an HPLC system onto an observation airplane. Concentrations of hydroperoxides in the high-altitude atmosphere were measured using an HPLC system aboard large NASA airplanes, such as the DC-8 and P3-B aircrafts (O'Sullivan et al., 2004; Snow et al., 2007). However, such large aircrafts are difficult to charter and, thus, are not suitable for local observation. In this study, we used a helicopter to measure hydroperoxides in the high-altitude atmosphere. A helicopter seems to be useful for topical observation (e.g., Imhoff et al., 1995; Matsunaga et al., 2010; Siebert et al., 2010).

The aim of this paper is to present a new method of measuring hydroperoxide in the high-altitude atmosphere using helicopter and an HPLC system in a laboratory. We report the preliminary results of observations during summers and discuss the behaviors of hydroperoxides and the potential capacity for the oxidation of $SO_2$ over a rural site near the coast of the Japan Sea, where a large amount of air pollution is transported from Asia as well as from industrial regions in Japan.

## 2. Observation

### 2.1. Observation site

A helicopter was used for observation over Imizu City, where Toyama Prefectural University (16 m above sea level) is located, on a rural site in Toyama Prefecture, Japan (Fig. 1) during summers (or early autumns) from 2010 to 2014. The observation site is located on the coast of the Japan Sea in central Japan, where air pollution is actively transported from Asia as well as Japan (Watanabe et al., 2006a, 2011a; Watanabe and Honoki, 2013; Iwamoto et al., 2016). Toyama Prefecture has a steep topography within a horizontal distance of 50 km. The observation site is also located approximately 50 km windward of Mt. Tateyama (altitude, 3015 m) (Fig. 1).

We have made many observations at Mt. Tateyama (Kume et al., 2009; Watanabe et al., 2010, 2011a, 2011b, 2011c, 2012; Watanabe and Honoki, 2013; Uehara et al., 2015). Strong acidic fog or cloud water and high levels of air pollutants have been detected. A serious decline in the forest in the vicinity of Mt. Tateyama has been seen. Especially, serious are the harmful influence of photochemical oxidants, which have increased widely over East Asia, on the vegetation (Kume et al., 2009). Observations of vertical profiles of air pollutants, such as hydroperoxides and $O_3$, over Imizu City, on the windward side of Mt. Tateyama, are important for evaluating their influence on the ecosystem of a mountainous site in central Japan, where the atmospheric environment is highly affected by extensive air pollution in East Asia.

### 2.2. Helicopter observation

We used a Robinson R44 helicopter owned by the Advanced Air Corp (http://www.addair.jp/), which is a four-seat light helicopter with a semi-rigid two-bladed main rotor, a two-bladed tail rotor, and a skid landing gear. The cost of chartering this small helicopter is relatively low. Observations were performed in the afternoon (approximately 13 H Japan Standard Time (JST; UTC + 9 H) to 15 H JST) on 23 August 2010, 7 June 2011, 31 August 2012, 7 August 2013 and 3 September 2014, when the sky was clear or partially cloudy. Two flight observations were made both in the morning (about 10 H JST to 12 H JST) and the afternoon on August 23, 2010. Hydroperoxides in the atmosphere were collected every 2000 ft (approximately 600 m) to an altitude of 10,000 ft (approximately 3000 m) during horizontal circular flights (in a radius of approximately 5 km). The flight speed was approximately 110 km/h. The ranges of the flights were small and are not illustrated in Fig. 1.

A mist chamber made of Pyrex glass (Hatakeyama et al., 1993; Takami et al., 2003) was used to sample of the hydroperoxides. The same type of mist chamber has been used by Takami et al. (2003), Chen et al. (2008) and Chutteang et al. (2012) to sample hydroperoxides. A diluted $H_3PO_4$ solution (pH = 3.5) added to a small amount of formaldehyde in the mist chamber was nebulized by flowing sample air and dissolved water-soluble gaseous compounds, such as hydroperoxides, into the solution. The mist chamber was placed on the front passenger seat, and the sampling was performed at 4.0 L $min^{-1}$ for 10 min through 6 mm ID Teflon tubing (1 m length). To prevent the photolysis of hydroperoxides during the sampling, the mist chamber was shielded by aluminum foil. Due to the high solubility of hydroperoxides, the trapping yield of $H_2O_2$ by the mist chamber is approximately 100%. However, the trapping yield of MHP, whose Henry's law constant (M $atm^{-1}$) is much lower than that of $H_2O_2$ (Seinfeld and Pandis, 1998), is roughly estimated to be 60%. According to Klippel et al. (2011), the trapping efficiency of MHP into a stripping solution is approximately 60% whereas that of $H_2O_2$ is 100%. A 50–60% collection efficiency of MHP relative to that of $H_2O_2$ has been reported (Jackson and Hewitt, 1996; Walker et al., 2006). Therefore, we calculated the trapping efficiency of 60% for MHP and treated the measured MHP concentrations as semi-quantitative values in this paper.

After each hydroperoxide sampling, the helicopter descended at once to a height of approximately 5 m on the campus of Toyama Prefectural University, and the polyethylene bottle that contained the sampling solution was transported to our laboratory. The sample solution was immediately analyzed using an HPLC system (Jasco, LC-2000 Plus) equipped with a separate column (Jasco, Crestpack C18T-5), preceded by a guard column (Jasco Crestpack C18T-5P) that separates $H_2O_2$ and organic hydroperoxides, such as MHP. The columns were kept at 5 °C. A peroxidase enzyme fluorescence method (Lazrus et al., 1985, 1986) was adopted to detect hydroperoxides with a fluorescence detector (Jasco, FP-2020 Plus). The detailed analytical method is described in Iwama et al. (2011) and Watanabe et al. (2012).

After transporting sample, the helicopter immediately ascended to the higher altitude, and hydroperoxides were collected again. After the next sampling, the helicopter immediately descended near ground level on the campus. The sample was transported to our laboratory and, once again, analyzed at once using our system.

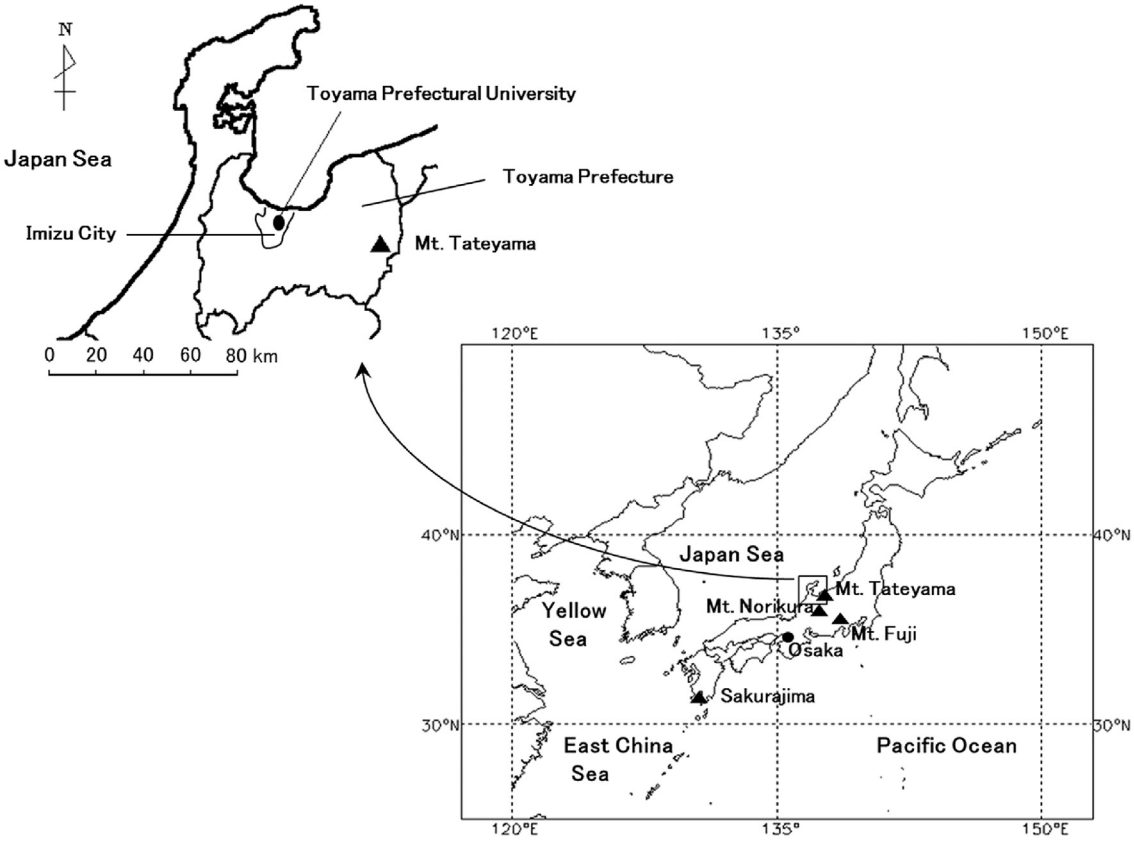


**Fig. 1.** Map of Japan showing the location of Toyama Prefectural University, Imizu City, Toyama Prefecture and Mt. Tateyama.

With the helicopter, we could measure hydroperoxides in the high-altitude atmosphere using the HPLC system in our laboratory within 5–10 min after sampling. The total sampling flight time at one observation (5 altitudes) was approximately 2 h.

The concentrations of $O_3$, $SO_2$ and $NO_X$ in the air were also measured using an ultraviolet absorption technique ($O_3$ analyzer, model OA-683, Kimoto Electric Corporation), an ultraviolet fluorescence technique ($SO_2$ analyzer, model SA-633, Kimoto Electric Corporation), and a chemiluminescence technique ($NO_X$ analyzer, model NA-623, Kimoto Electric Corporation), respectively. The $O_3$ analyzer was used to measure $O_3$ over the Pacific Ocean (Watanabe et al., 2005). The commercial $NO_X$ analyzer used cannot avoid the interference of other nitrogen compounds, such as $HNO_3$ gas and PAN (Watanabe et al., 2011b); therefore, the data measured using the $NO_X$ analyzer were treated as $NO_X^*$. The analyzers were placed in the rear seat of the helicopter. Four mm-ID Teflon tubes (approximately 2 m in length) were used to draw ambient air. Unfortunately, the $NO_X$ analyzer, which takes time to warm-up, could not be loaded on 23 August 2010, 7 August 2013 and 3 September 2014. The data were recorded every minute, and 7–10 min averaged data at each altitude were plotted.

Meteorological data (temperature, dew point temperature and relative humidity) were also measured using temperature relative humidity data loggers (HOBO Pro V2 model U23-001, Onset Corporation) attached to the bottom of the helicopter to avoid direct sunlight. Abrupt increases in $SO_2$ and $NO_X^*$ (or an abrupt decrease in $O_3$) were not detected during the sampling of hydroperoxides; therefore, the sampling air was not affected by the helicopter's exhaust. Desmet et al. (1995) also reported that the measurements of atmospheric pollutants, such as $O_3$, $NO_x$, $SO_2$, and dust on board helicopters, were not subject to contamination by the turbine exhaust. After all, a helicopter is useful for local observation in the high-altitude atmosphere.

## 3. Results and discussion

### 3.1. Meteorological conditions

Surface weather charts at 09H JST on 23 August 2010, 7 June 2011, 31 August 2012, 7 August 2013 and 3 September 2014 are shown in Fig. 2. The sky was clear or partially cloudy in the observation days. Pressure patterns on 23 August 2010 and 31 August 2012, were typical of a summer monsoon in which central Japan was under the influence of the Pacific high pressure. Southerly or southwesterly winds were predominant. On the other hand, central Japan was to the north of the seasonal rain front (the Baiu front) on 7 June 2011, and under the influence of the continental air mass. The rainy season (Baiu) in central Japan usually lasts from June to July and mid-summer begins after the Baiu. On 7 August 2013, the Pacific high moved to the southwest, and a westerly wind from the Asian continent was predominant. Air pollutants were actively transported from China to central Japan on 7 August 2013 (discussed below). A southerly wind was also predominant on 3 September 2014.

The vertical profiles of the meteorological elements (temperature, dew point temperature and relative humidity) over Imizu City are presented in Fig. 3. The dew point temperature and relative humidity decreased abruptly at an altitude of 8000 ft on 23 August 2010, in the morning and on 7 June 2011 (Fig. 3). The border between the atmospheric boundary layer and the free atmosphere might have existed at a height of approximately 2400 m on the two days. The boundary might have existed at altitudes of 4000 to

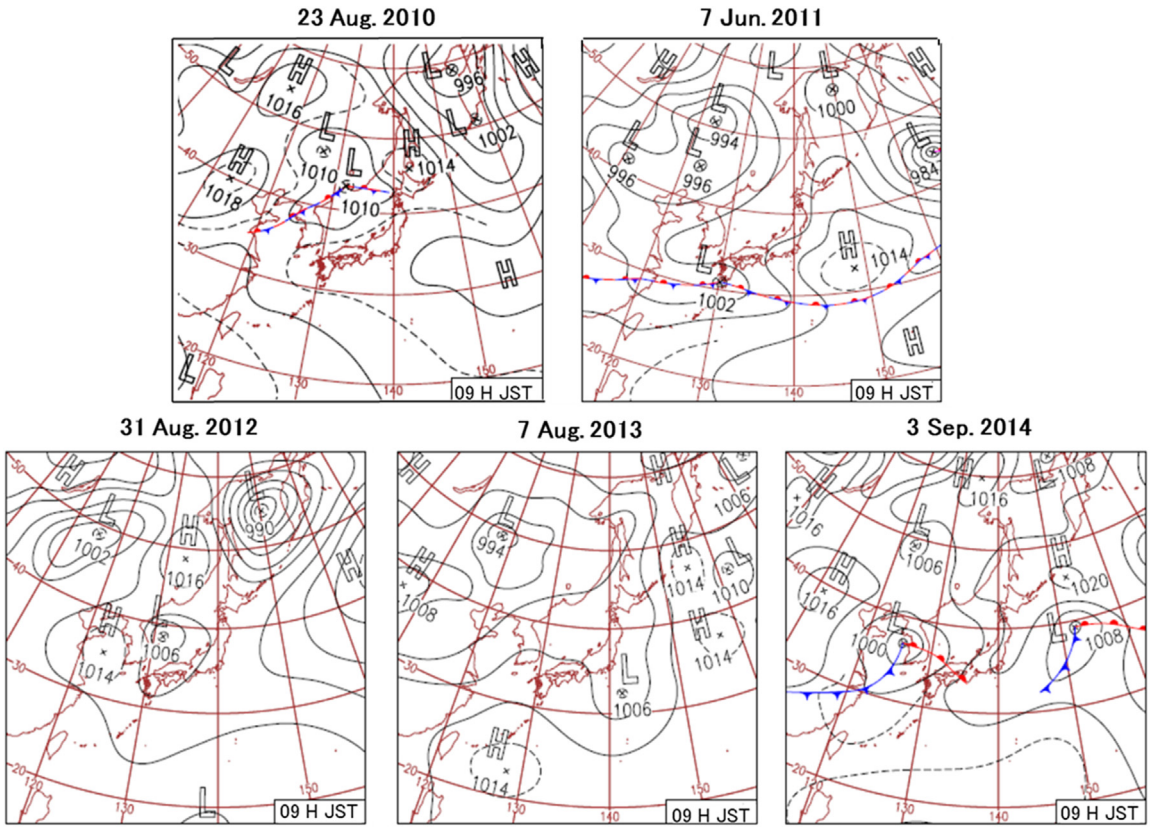


**Fig. 2.** Surface weather charts at 09H JST on 23 August in 2010, 7 June 2011, 31 August 2012, 7 August 2013 and 3 September 2014.

6000 ft on 7 August 2013. On 7 June 2011, the dew point temperature was lower, which means the water vapor was lower due to the influence of the continental air mass. The temperature was also relatively low on 7 June 2011 (Fig. 3).

### 3.2. Vertical profiles of trace gases

A summary of the concentrations of trace gases ($H_2O_2$, MHP (semi-quantitative), $O_3$, $SO_2$ and $NO_X$*) over Imizu City, Toyama Prefecture, Japan, in the afternoon during summers from 2010 to 2014 is presented in Table 1. $H_2O_2$ concentrations ranged from 0.2 to 6.7 ppb. Vertical profiles of the atmospheric pollutants over Imizu City on 23 August 2010, 7 June 2011, 31 August 2012, 7 August 2013 and 3 September 2014 are shown in Fig. 4. As mentioned above, $NO_X$* measurements were made only on 7 June 2011 and 31 August 2012. Unfortunately, trace gases could not be measured above 8000 ft on 31 August 2012, and at altitudes of 2000 and 10,000 ft on 3 September 2014. Also, hydroperoxides could not be sampled at an altitude of 10,000 ft in the morning on 23 August 2010.

$H_2O_2$ concentrations were lowest at ground level, and the maximum concentrations were usually observed at altitudes of 6000 to 8000 ft (about 1800 to 2400 m) (Fig. 4). The concentrations of $H_2O_2$ above 2000 ft were similar on 7 June 2011. The measured $H_2O_2$ concentrations are comparable to the concentrations of hydroperoxides at high mountainous sites in Japan and China during summers (Watanabe et al., 1995; Ren et al., 2009). The high $H_2O_2$ in the high-altitude atmosphere seems to be due to high ultraviolet (UV) radiation and low nitric oxide (NO) which prevents the combination of two hydroperoxy radicals ($HO_2$) and the formation of $H_2O_2$ (Seinfeld and Pandis, 1998; Lee et al., 2000; Acker et al., 2008; Hua et al., 2008). The lowest $H_2O_2$, near the ground level, is due to low ultraviolet (UV) radiation and a high concentration of $NO_X$, which is usually highest at ground level because $NO_X$ is the primary air pollution. Measured $NO_X$* concentrations were highest on the ground and were lower at high altitudes (Fig. 4). The vertical profiles of $H_2O_2$ are quite similar to those over the United States as reported by Kleinman and Daum (1991). MHP (semi-quantitative) concentrations were also lowest at ground level and higher in the high-altitude atmosphere (Fig. 4).

The concentrations of $O_3$ were high in the high-altitude atmosphere in the morning on 23 August 2010 (Fig. 4). However, the vertical profiles of $O_3$ were relatively similar except at an altitude of 2000 ft in the afternoon on 23 August 2010. The vertical mixing of the atmosphere developed in the afternoon. The concentrations of $SO_2$ were usually highest near ground level. On 3 September 2014, the $SO_2$ concentrations in the high-altitude atmosphere were higher than those of the surface $SO_2$; the concentration of $SO_2$ at the altitude of 8000 ft was approximately 2.5 ppb. On the other hand, the $SO_2$ concentration was approximately 0.2 ppb on the ground (Fig. 4). Air pollution was transported to high-altitudes over Imizu City on 3 September 2014.

$H_2O_2$ concentrations at the lower altitudes (<2000 ft) were higher in the afternoon than in the morning on 23 August 2010 (Fig. 4). The concentration of $H_2O_2$ at a lowland (plain) site is usually highest in the afternoon and lowest at night and in the early morning (e.g., Sakugawa and Kaplan, 1989; Watanabe and Tanaka, 1995; Hua et al., 2008; Chutteang et al., 2012). $H_2O_2$ in the polluted atmosphere is produced by photochemical reactions in the daytime (Sakugawa and Kaplan, 1989; Watanabe and Tanaka, 1995). The mean concentration of $H_2O_2$ at altitudes lower than 8000 ft in the afternoon (2.8 ppb) was the same as that in the morning. The daytime increase in $H_2O_2$ near ground level in Imizu City may be mainly due to the vertical mixing of the atmosphere.

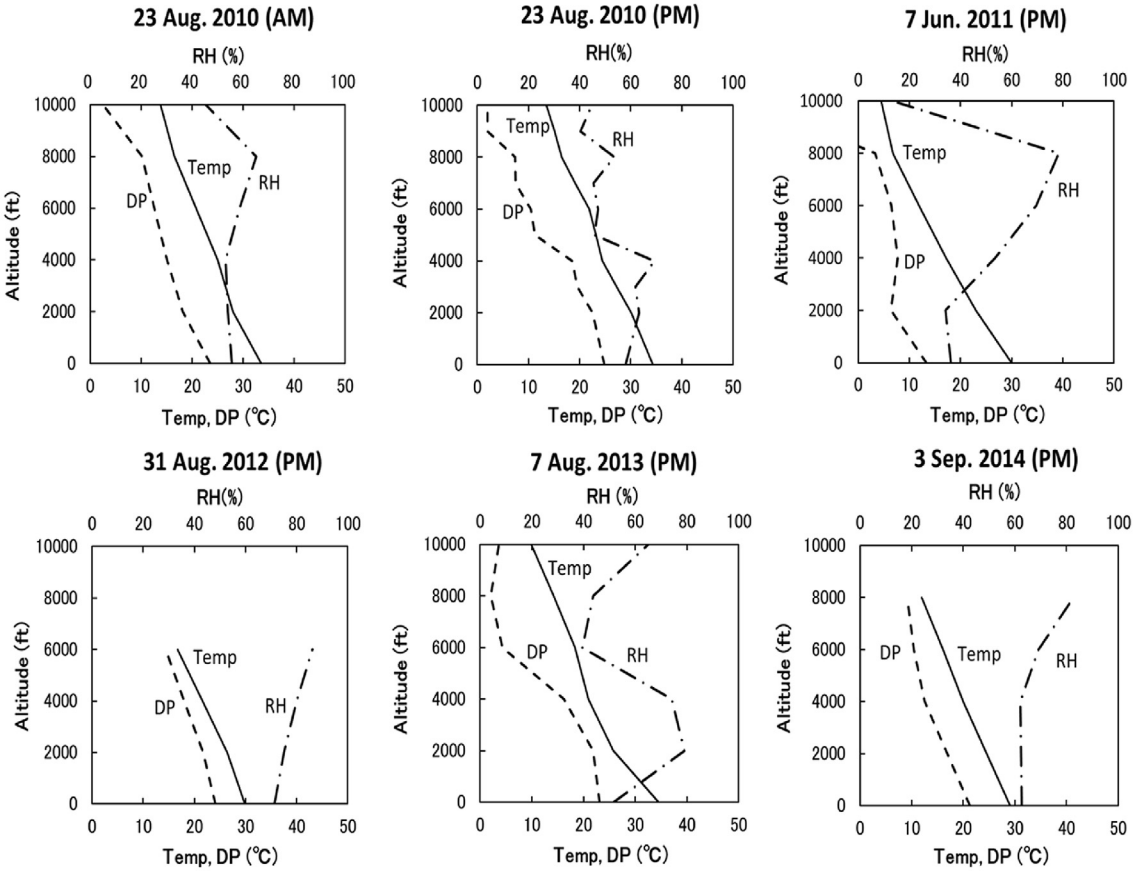


**Fig. 3.** Vertical profiles of temperature (Temp), dew point temperature (DP) and relative humidity (RH) over Imizu City, Toyama Prefecture, Japan in the morning (AM) and afternoon (PM) on 23 August in 2010 and in the afternoon (PM) on 7 June 2011, 31 August 2012, 7 August 2013 and 3 September 2014.

**Table 1**
Summary of the concentrations of trace gases ($H_2O_2$, MHP (semi-quantitative), $O_3$, $SO_2$ and $NO_X$*) over Imizu City, Toyama Prefecture, Japan in the afternoon during summers. The units of the concentrations are ppb. N and ND denote the number of hydroperoxide samples and non-data, respectively.

| Date | N | $H_2O_2$ | MHP | $O_3$ | $SO_2$ | $NO_X$* |
|---|---|---|---|---|---|---|
| 23 Aug. 2010 | 6 | 2.0–3.6 | 0.3–0.5 | 40–60 | 1.1–4.5 | ND |
| (Mean) | | (2.8) | (0.4) | (46) | (2.7) | |
| 7 Jun. 2011 | 6 | 0.7–2.5 | 0.3–0.7 | 60–76 | 0.9–3.3 | 0.6–8.3 |
| (Mean) | | (1.9) | (0.6) | (69) | (1.8) | (3.0) |
| 31 Aug. 2012 | 4 | 0.5–2.8 | 0.3–0.8 | 29–45 | 0.2–2.0 | 2.6–18 |
| (Mean) | | (2.1) | (0.6) | (37) | (1.1) | (7.1) |
| 7 Aug. 2013 | 6 | 1.8–6.7 | 0.6–3.0 | 54–74 | 0.1–2.2 | ND |
| (Mean) | | (4.9) | (1.9) | (66) | (0.9) | |
| 3 Sep 2014 | 4 | 0.2–3.0 | 0.1–1.2 | 37–55 | 0.2–2.6 | ND |
| (Mean) | | (1.8) | (0.7) | (48) | (1.5) | |

### 3.3. Transport processes of air pollution and $H_2O_2$ concentrations

Examples of 80-h backward trajectories by the Hybrid Single-Particle Lagrangian Integrated Trajectory 4 model (Stein et al., 2015) (NOAA Air Resources Laboratory, Silver Spring, Maryland, 1997, available at http://www.arl.noaa.gov/ready/hysplit4.html) are illustrated in Fig. 5. The ending heights for the calculations were 1800 m (6000 ft), 2400 m (8000 ft) and 3000 m (10,000 ft) on 23 August 2010, 7 June 2011 and 7 August 2013, and 1200 m (4000 ft), 1800 m and 2400 m on 31 August 2012 and 3 September 2014. Air masses were transported from the south or southwest direction on 23 August 2010, 31 August 2012 and 3 September 2014. On the other hand, the air was derived from the Asian continent on 7 June 2011 and 7 August 2013. On 7 August 2013, the air mass was transported through the polluted areas of the continent, especially from the coasts of the Yellow Sea, where anthropogenic emissions are high (Ohara et al., 2007). Many air pollutants might have been transported to the observation site from industrial areas in China on 7 August 2013.

The concentrations of $H_2O_2$ and $O_3$ at altitudes of 6000 and 8000 ft on 23 August 2010, 31 August 2012 and 3 September 2014, when central Japan was under the influence of maritime air masses, were about 2.3–3.9 ppb (mean 3.0 ppb) and 29–55 ppb (mean 45 ppb), respectively. The background $O_3$ concentration over central Japan in the summer is approximately 40 ppb (near 45 ppb) (Tanimoto, 2009). Therefore, the standard concentration of $H_2O_2$ over rural sites in central Japan may be about 3 ppb in the summer. Significantly high concentrations of $H_2O_2$ (5.8–6.7 ppb) and $O_3$ (70–73 ppb) were observed on 7 August 2013 (Fig. 4), when air pollution was transported from China. Pochanart et al. (1999) reported that a high $O_3$ concentration was observed at a remote site in Japan under the influence of the continental air mass in the summer. Koga and Tanaka (1993) reported that when $O_3$ concentration rises 1.5 times, $H_2O_2$ increases by a factor of two in the box model. MHP (semi-quantitative) was also high on 7 August 2013 (Fig. 4). Photochemical oxidants, such as $O_3$ and hydroperoxides, were actively produced during the long-range transport of the polluted air.

Low $H_2O_2$ levels during the inflow of air pollution have been frequently reported (e.g. Jackson and Hewitt, 1996; Sauer et al., 1997; Morgan and Jackson, 2002; Walker et al., 2006; Ren et al., 2009). A decrease in $H_2O_2$ might be due to high $NO_X$. However,

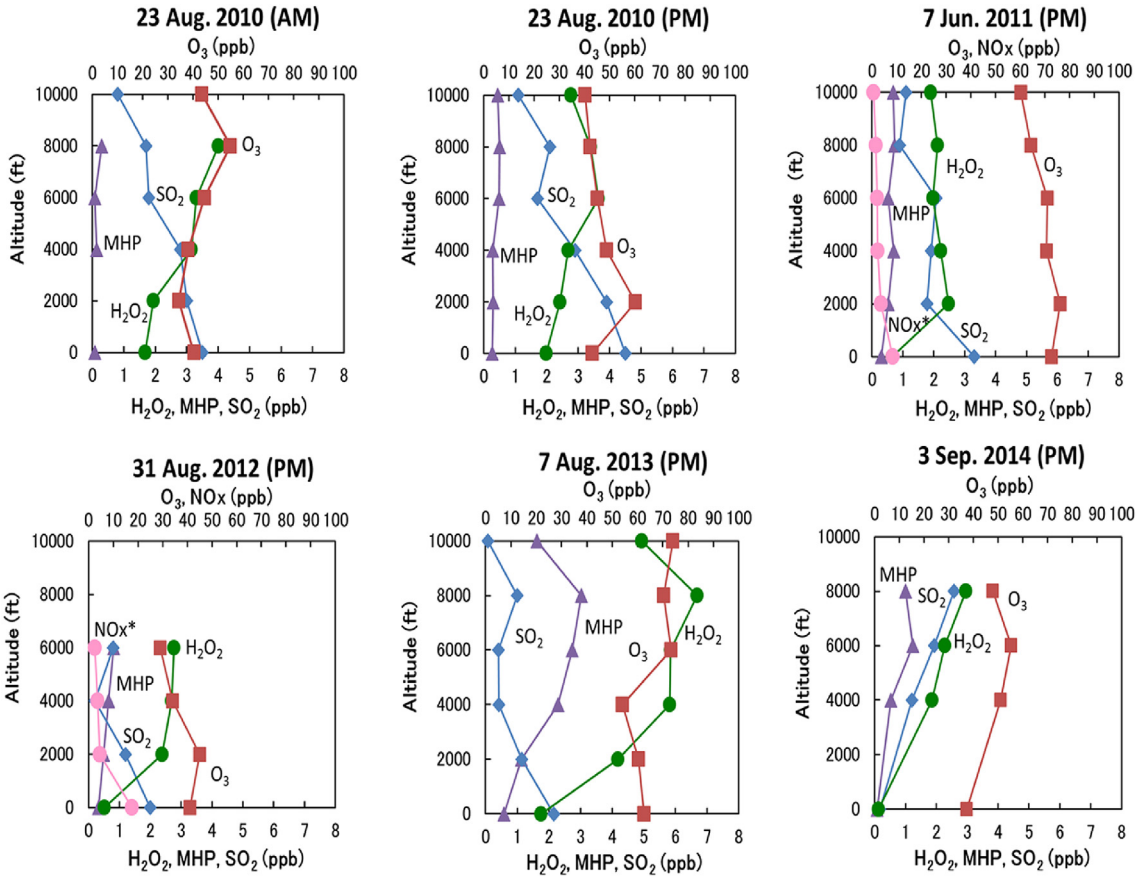


**Fig. 4.** Vertical profiles of $H_2O_2$, MHP (semi-quantitative), $SO_2$, $O_3$ and $NO_X$* over Imizu City, Toyama Prefecture, Japan in the morning (AM) and afternoon (PM) on 23 August in 2010 and in the afternoon (PM) on 7 June 2011, 31 August 2012, 7 August 2013 and 3 September 2014.

$NO_X$ concentrations were relatively low in the case of 7 August 2013 (unfortunately, measurements of $NO_X$* were not made directly). $NO_X$ at ground level in Imizu City was not high on 7 August 2013 (unpublished data). As a result, hydroperoxide formation was not suppressed, and the high concentrations of $O_3$ might have led to the increase in $HO_2$ and, hence, to the increase in $H_2O_2$. Similar phenomena have been reported in several studies (Takami et al., 2003; Hua et al., 2008). Takami et al. (2003) showed that high concentrations of $O_3$ and hydroperoxides were observed at the foot of a mountainous site in Japan when polluted air masses were transported from urban areas. Relatively high levels of $H_2O_2$ and MHP were found in polluted air at a rural site in southern China (Hua et al., 2008).

According to Chen et al. (2010) and Na-Ngern et al. (2014), $O_3$ combined with high hydroperoxides (>3 ppb) causes severe damage to plants. Trans-boundary pollution from the Asian continent in the summer may seriously influence the ecosystem at high-elevation sites. $SO_2$ concentrations were relatively low on 7 August 2013 (Fig. 4). Most of the $SO_2$ emitted from China seemed to be oxidized to sulfate by OH in gas phase during long-range transport. High concentrations of fine particles were observed at Toyama Prefectural University (Imizu City) on 7 August 2013 (unpublished data).

The mean $O_3$ concentration was highest on 7 June 2011, when central Japan was under the influence of a continental air mass (Table 1). The $O_3$ concentration in the continental air mass is higher than that in the maritime air mass (Watanabe et al., 1996: Pochanart et al., 1999). However, the $H_2O_2$ concentrations were not higher, and the $NO_X$* concentrations were lower than those on 31 August 2012 (Table 1). The low dew point (low water vapor) and relatively low temperature (Fig. 3) might have suppressed the formation of hydroperoxides. The concentrations of $SO_2$ on 7 June 2011 were higher than those on 31 August 2012 and 7 August 2012 (Table 1). The $SO_2$ seemed to be transported from the Asian continent.

High concentrations of $SO_2$ were observed on 23 August 2010 (Fig. 4). According to the backward trajectories, the air mass was transported from near Sakurajima volcano, the most active volcano in Japan (Fig. 5). The annual frequency of Sakurajima's eruptions exceeds 1000 times from 2010, and the influence of the smoke of Sakurajima has been observed in central Japan (Watanabe et al., 2015). The high $SO_2$ might have been derived from the eruption of Sakurajima. The high concentration of $SO_2$ at an altitude of 8000 ft on 3 September 2014 (Fig. 4) was due to air pollution from urban areas, such as Osaka City (Fig. 5).

### 3.4. Potential capacity for oxidation of $SO_2$

At altitudes of lower than 4000 ft on 23 August 2010, the $H_2O_2$ concentrations were lower than the $SO_2$ concentrations ($[H_2O_2] < [SO_2]$); this condition is called *oxidant limitation*, which means a nonlinear relationship between $SO_2$ emission and sulfate deposition (Kleinman and Daum, 1991). All profiles in Fig. 4 show the condition of $[H_2O_2] < [SO_2]$ at the surface. If fog occurs near the ground, $SO_2$ oxidation and the formation of sulfuric acid ($H_2SO_4$) in the aqueous phase are suppressed.

However, the concentrations of $H_2O_2$ were higher than those of $SO_2$ ($[H_2O_2] > [SO_2]$) above a height of 2000 or 4000 ft on

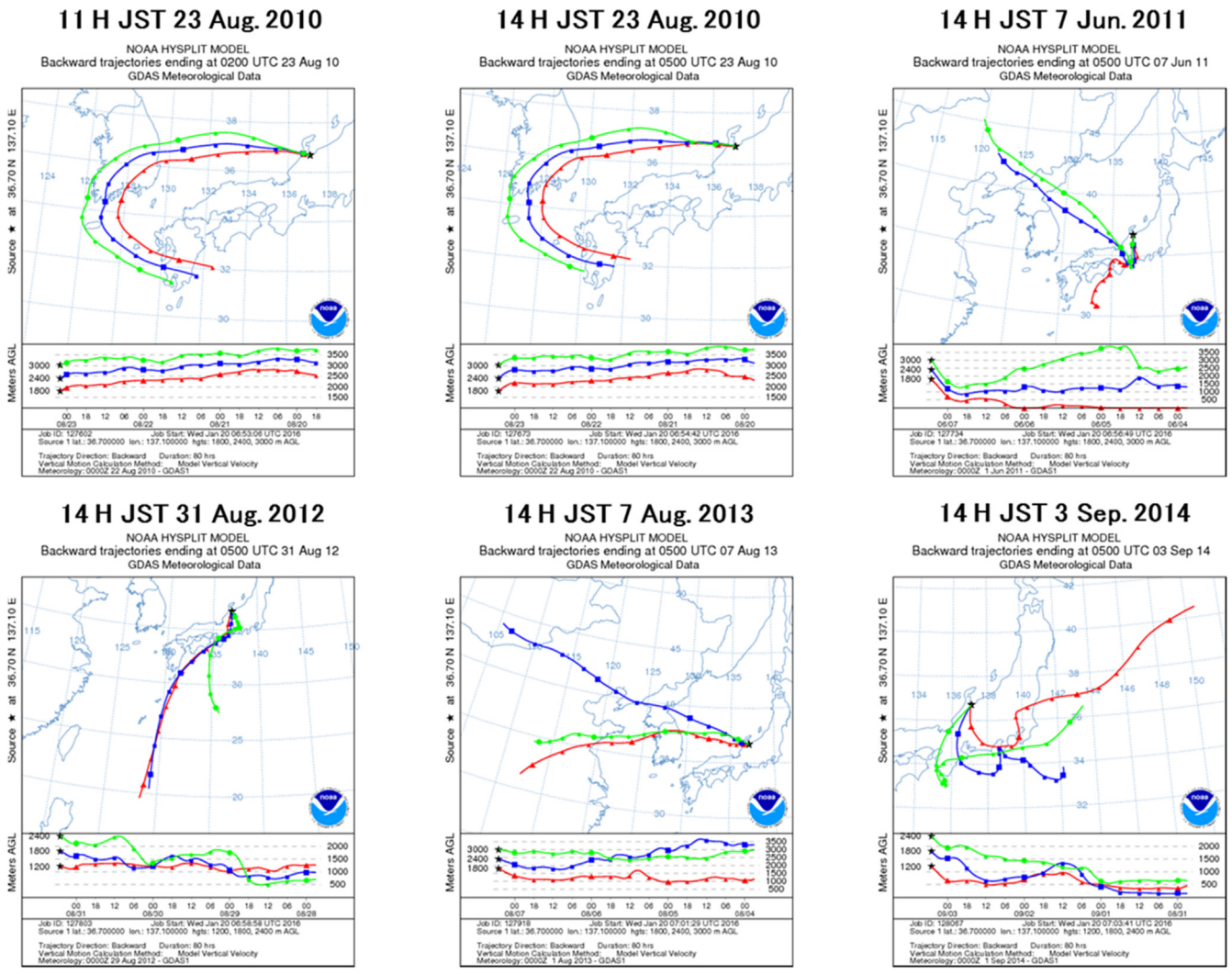


**Fig. 5.** Results of 80-h backward trajectory analysis; the ending times are 11 H JST (2 H UTC) and 14 H JST (5 H UTC) on 23 August in 2010, and 14 H JST (5 H UTC) on 7 June 2011, 31 August 2012, 7 August 2013 and 3 September 2014.

observation days (Fig. 4), where the potential capacity of $SO_2$ oxidation in the aqueous phase is large. Under the condition of $[H_2O_2] > [SO_2]$, if all $SO_2$ is oxidized by $H_2O_2$, excessive $H_2O_2$ exists in clouds. High concentrations of hydroperoxides (>50 μM) in cloud or fog water have been observed frequently during summers or early autumn at Murododaira (altitude, 2450 m) near the summit of Mt. Tateyama, located approximately 50 km east (downwind) from Imizu City (Fig. 1) (Watanabe et al., 2010). High concentrations of hydroperoxides in cloud water were also seen during summers and early autumn near the summit of Mt. Norikura (altitude, 2770 m) (Watanabe et al., 1999, 2001b) and at the top of Mt. Fuji (altitude, 3776 m) (Watanabe et al., 2006b). If the $SO_2$ concentration in the high-altitude atmosphere rises in the summer and early autumn, even if slightly, acidic fogs may easily be produced in circumstances with sufficient oxidant at high elevations in central Japan.

## 4. Summary

Concentrations of hydroperoxides as well as the concentrations of $SO_2$, $O_3$ and $NO_X$* in the high-altitude atmosphere over a rural site near the coast of the Japan Sea, Imizu City, Toyama Prefecture, Japan, were measured using a helicopter (the Robinson R44 helicopter) on 23 August 2010, 7 June 2011, 31 August 2012, 7 August 2013 and 3 September 2014. Hydroperoxides were collected in a mist chamber, and the sample solution was immediately transported to our laboratory. We could measure the concentrations of hydroperoxides in the high-altitude atmosphere using the HPLC system in our laboratory within 5–10 min after the sampling.

$H_2O_2$ concentrations were lowest at the ground, and the highest concentrations were usually detected at altitudes of 6000 and 8000 ft. On the other hand, the concentrations of $SO_2$ and $NO_X$* were highest at ground level, except on 3 September 2014. MHP (semi-quantitative value) was also lowest at the surface and higher in the high-altitude atmosphere. Significantly high concentrations of hydroperoxides were observed on 7 August 2013, when air pollutants were transported to the observation site from industrial areas of China. Trans-boundary pollution in the summer seriously influence the ecosystem at high elevation sites in central Japan. The concentrations of $H_2O_2$ were higher than those of $SO_2$ above 4000 ft where the potential capacity of $SO_2$ oxidation in the aqueous phase is large.

The sampled air was not affected by the helicopter's exhaust. A helicopter is useful for measurements of hydroperoxides in the high-altitude atmosphere using an HPLC system in a laboratory. More observations are required to elucidate the atmospheric environment, such as the oxidation capacity of $SO_2$, over Japan, where the background $O_3$ has significantly changed.

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